Photochemistry and molecular ions in carbon-rich circumstellar envelopes

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Summary. Our earlier theory of ionization of C-rich circumstellar envelopes based on the photochemical model is extended to include the temperature dependence of ion-molecule reactions with polar molecules, particularly HCN, and line self-shielding of CO dissociating radiation. The results are applied to the abundances of HCO^+ and HNC in C-rich circumstellar envelopes. With standard parameters for IRC + 10216, the model is found to be consistent with the new upper limit to the antenna temperature of the $J = 1 - 0$ line of HCO^+ obtained with the IRAM 30-m telescope. The photochemical model provides a natural explanation of the relatively large ratio of HCN to HNC observed for C-rich circumstellar envelopes, and good agreement is obtained for the $H^{13}CN$/HNC antenna temperature ratio measured for IRC + 10216.

Key words: circumstellar matter – ionization – molecules

1. Introduction

The chemistry of circumstellar envelopes (CSEs) of cool evolved stars is of considerable interest in the context of millimetre and infrared observations of a wide variety of molecules (see, e.g., the reviews by Omont 1985 and by Glassgold and Huggins 1986). In a recent paper (Glassgold, Lucas, and Omont 1986, henceforth referred to as GLO), we developed a theory of ionization of C-rich CSEs with particular reference to the well observed star IRC + 10216. The theory was based on the photochemical model, supplemented by cosmic ray ionization. According to this model, strongly bound molecules entering the CSE (beyond the region of dust formation) are destroyed by penetrating interstellar ultraviolet (UV) radiation. In addition to providing cut-offs in the spatial distributions of circumstellar molecules, photodestruction generates families of strongly interacting radicals, atoms, and ions. It was shown in GLO that ion-molecule reactions are the most important reactions in the cool outer parts of C-rich CSEs. The main ions are $C_2H_2^+$ (produced by photoionization of acetylene), C^+ (produced by photoionization of carbon generated in the photochains of CO, C_2H_2, HCN, etc.),

and a series of ions produced by cosmic rays such as H_3^+, HCO^+, HN_2^+, $C_2H_3^+$, and H_2CN^+.

It was suggested in GLO that the $J = 1 - 0$ line of HCO^+ might be detected in IRC + 10216 with a sensitive search near 89.2 GHz. Lucas et al. (1986) obtained an upper limit of 20 mK for the brightness temperature of this line with the new IRAM 30-m telescope, equivalent to almost a factor of 5 less than an earlier limit (Johansson et al., 1984). One objective of this paper is to evaluate this result in terms of our model of circumstellar chemistry and ionization.

In this paper we improve the GLO model by incorporating recent advances in our understanding of ion-molecule reactions and CO line self-shielding. The most important aspect of the new treatment of ionic reactions is the temperature dependence of reactions with polar molecules (Adams et al., 1985) and dissociative recombination of H_3^+ and HCO^+ (Adams and Smith 1987). The temperature is expected to vary by one or two orders of magnitude in the CSE (Kwan and Linke 1982), and ionic reactions are sensitive to the low temperature conditions of the outer envelope. Self-shielding of CO was invoked in GLO to argue that C^+ is not significantly produced from the CO photochain until the radial distance r exceeds the cut-off parameter r_c ($\sim 10^{18}$ cm for IRC + 10216) introduced by Morris and Jura (1983). A more detailed study of CO line self-shielding (Mamon et al., 1987) indicates, however, that C^+ production from CO occurs well before r_c and can compete with ionization produced from the acetylene chain.

The large range in the HCN/HNC ratio measured in interstellar clouds has been a puzzle for interstellar chemistry for some time (see, for example, the review by Irvine et al. 1985). The ratio of unity for cool clouds is consistent with ion-molecule chemistry, as first predicted by Watson (1974). However, the much larger ratios found in OMC-1, about 250 for the plateau source and 20 for the ridge, have no satisfactory explanation at the present time. For IRC + 10216, Olofsson et al. (1982) have derived a value of ~ 250 for the HCN/HNC abundance ratio. This value is small compared to predictions based on thermal equilibrium considerations, and we will show that the HCN/HNC ratios found in C-rich CSEs can be understood in terms of ion-molecule chemistry.

In the next section we describe the various changes in our theory of ionization and chemistry of C-rich CSEs. The main results of these changes will be presented in Sect. 3, which includes a discussion of the new observational limits on HCO^+ for IRC + 10216 and an estimate of the abundance of HNC and its line intensity. The paper is concluded with a brief summary.

2. Developments in the model

The alterations in the GLO model that are described here mainly produce quantitative rather than qualitative changes in the results. We refer to GLO for the physical basis and rationale of the model, except where significant changes are made, and continue to use the "standard" parameter set of GLO, given in Table 1 in abbreviated form.

Adams et al. (1985) have recently pointed out that reaction rates for ion polar molecule reactions decrease with increasing temperature below 300 K, and suggest that rate coefficients as large as $10^{-7}\,cm^{-3}\,s^{-1}$ may be appropriate for cold molecular gas (T $\sim$ 10 K). This increase is expected from theory (Clary 1985, and earlier work cited therein and in Herbst and Leung 1986) and has been verified in laboratory experiments (Adams and Smith 1987).

Table 2 gives new and revised reaction rate coefficients; it supplements the first part of Table 3 in GLO (and follows the same numbering system). Ionic reactions with HNC are assumed to be the same as for HCN. The temperature dependence of all

ion polar molecule reaction rate coefficients have been represented by

$$k(T) = k(300\,\mathrm{K})(300/T)^n \tag{1}$$

with $n \simeq 0.65$, our fit to the measurements for reaction No. 4. Ion molecule reactions with C_2H were included in order to determine whether they could reduce the abundance of C_2H below the prediction of the photochemical model (Huggins and Glassgold 1982a). Detailed analysis of the radio observations of C_2H lines in IRC + 10216 (Huggins et al., 1984, Truong-Bach et al., 1986) indicates that agreement with the model requires a much smaller abundance of C_2H_2 than is inferred from infrared absorption measurements. The same motivation lay behind the introduction of the neutral reaction No. 21 between C_2H and C_2H_2.

Most other reaction rate coefficients are the same as in GLO, with the following exceptions and additions. The photodissociation rate of HNC is assumed to be the same as for HCN, i.e. $7\,10^{-10}\,s^{-1}$. The recombination rate of HCO^+ is represented by $2.3\,10^{-5}\,T^{-1}\,cm^3\,s^{-1}$, consistent with both old (Leu et al., 1973) and new (Smith and Adams 1984) laboratory measurements. The upper limit to the H_3^+ recombination rate constant, $2\,10^{-8}\,cm^3\,s^{-1}$, has been replaced by the much smaller upper limit recently obtained by Smith and Adams (1985), $2\,10^{-11}\,cm^3\,s^{-1}$, and a temperature dependence $(300/T)^{0.5}$. Recombination of H_3^+ at this level is actually unimportant, even near the edge of the CSE where it is destroyed by proton transfer with CO and then with O.

We have now included photodissociation of CO using a theoretical treatment of CO line self-shielding (Mamon, et al., 1987). The contribution of the CO photochain to C^+ now begins to dominate for $r > 3 \times 10^{17}\,cm$. Because this is beyond the region of greatest chemical activity, the qualitative conclusion of GLO holds, i.e. CO line self-shielding makes only a quantitative

Table 1. Standard model for IRC + 10216

Distance	$d = 200\,pc$
Expansion velocity	$V = 16\,km\,s^{-1}$
Mass loss rate (total hydrogen)	$\dot{M} = 4\,10^{-5}\,M_\odot\,yr^{-1}$
Gas density, $n = Cr^{-2}$	$C = 7.5\,10^{37}\,cm^{-1}$
Abundances (relative to total hydrogen):	
CO	$3\,10^{-4}$
C_2H_2	$3\,10^{-5}$
HCN	$6\,10^{-6}$
Gas kinetic temperature	$T = 74\,K\,(r_{16})^{-0.79}$

Table 2. New or revised reaction rates[a,b]

Reaction	Rate coefficients at 300 K (cm^3 s^{-1})	References[d]
4. $H_3^+ + HCN \longrightarrow H_2CN^+ + H_2$	$8.0\,10^{-9}$	ASC 85
6. $HCO^+ + HCN \longrightarrow H_2CN^+ + H_2$	$3.0\,10^{-9}$	AH 84
10. $C_2H_2^+ + HCN \longrightarrow H_2CN^+ + C_2H$	$2.4\,10^{-10}$	AH 84
$C_3H_2N^+ + H$	$1.2\,10^{-10}$	
11. $C_2H_3^+ + C_2H_2 \longrightarrow C_4H_3^+ + H$	$2.5\,10^{-10}$	AH 84
12. $C_2H_3^+ + HCN \longrightarrow H_2CN^+ + C_2H_2$	$6.0\,10^{-10}$	AH 84
14. $C^+ + HCN \longrightarrow CNC^+ + H$	$3.5\,10^{-9}$	H 77, DKF 86
18. $HCO^+ + C_2H \longrightarrow C_2H_2^+ + CO$	1.0×10^{-9}	
19. $C^+ + C_2H \longrightarrow C_3^+ + H$	1.0×10^{-9}	
20. $C_2H_2^+ + C_2H \longrightarrow C_4H_2^+ + H$	$1.0\,10^{-9}$	
21. $C_2H + C_2H_2 \longrightarrow C_4H_3 + H$	3.0×10^{-11}	LB 79[c]

[a] All ion-molecule reaction rates for HCN and C_2H are assumed to vary as $T^{-0.65}$, as measured for reaction No. 4. (See text.)

[b] All reactions for HNC are assumed to occur with the same rate coefficients as HCN.

[c] Allen et al. (1980) interpret the measured value of the rate coefficient at 300 K to imply an activation energy for this reaction of 360 K.

[d] References to laboratory measurements: ASC 85 – Adams, Smith, and Clary (1985); AH 85 – Anicich and Huntress (1984); DKF 86 – Daniel, Keim, and Farrar (1986); H 77 – Huntress (1977); LB 79 – Laufer and Bass (1979)

difference in the chemistry of C-rich CSEs. This is in contrast to O-rich CSEs, where CO is by far the major source of the C^+ ion (Mamon et al., 1986).

A new feature of the present model is the emphasis on the HCN photochain. Although its abundance is small compared to the dominant neutral molecules in C-rich CSEs, HCN can be important because many molecular ions are destroyed by HCN with large reaction rates, especially at low temperatures. The isomer HNC is produced by dissociative recombination of H_2CN^+,

$$e + H_2CN^+ \longrightarrow \begin{cases} HCN + H & b_1 \\ HNC + H & b_2 \\ CN + H_2 & b_3. \end{cases} \quad (2)$$
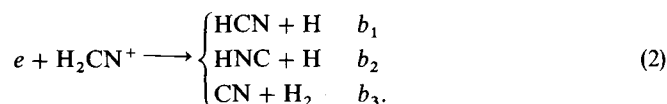
The branching ratios b_i have not been measured, and we have used the results of phase space calculations of Herbst (1978), $b_1 = b_2 = 0.25$ and $b_3 = 0.5$. The general considerations of Bates (1986) also support a large value for b_3. The H_2CN^+ ion is produced by proton transfer of other molecular ions with HCN,

$$MH^+ + HCN \longrightarrow H_2CN^+ + M \quad (3)$$
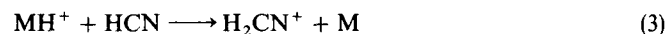
particularly $C_2H_2^+$. Thus, increased destruction of other molecular ions by HCN at low temperatures is accompanied by enhanced production of H_2CN^+, and then of HNC.

3. Results

We now present the results obtained with the revised chemical model, including variations in the standard model that test its stability to changes of parameters and assumptions.

3.1. Abundance and spatial distribution of molecular ions

The spatial variation of the abundances are familiar from previous studies (e.g. Huggins and Glassgold 1982, Huggins, et al., 1984, and GLO in particular): progenitor molecules are located toward the inside of the CSE, radicals and molecular ions in the middle (e.g. in the range $10^{16} - 10^{17}$ cm for the standard case), and C^+, N, and O on the outside. The spatial distributions of the *main* C-bearing species in the region of interest ($3\,10^{15} < r < 3\,10^{17}$ cm) are similar to Fig. 5a of GLO, and we only comment briefly on several quantitative changes. In GLO, the peak abundances of C_2H, C_2, and C are all about the same, $\sim 1.5\,10^{-5}$ for the standard model. In the new calculations, these abundances are reduced by about 2/3 and the peak abundance of C_2H is now the smallest, $\sim 9\,10^{-6}$. This reduction is due to the new reactions in Table 2 which destroy C_2H, particularly the neutral reaction No. 21 – if we assume there is no activation energy. Although this decrease is clearly insufficient to explain the radio observations of C_2H in IRC + 10216 in the context of the photochemical model (Huggins et al. 1984, Truong-Bach et al., 1986), it may suggest a possible resolution of the difficulty. The C_2H radical is generally chemically reactive with carbon and hydrocarbon molecules. If a substantial fraction of the carbon not in CO were incorporated into these species in the process of incomplete dust formation in the inner envelope, they might be able to destroy the bulk of the photochemically produced C_2H. However, there is no sign of a large enough abundance of carbon in such species, either in long chain molecules observed in the radio or in polycyclic aromatic hydrocarbons, whose presence would be observed by characteristic IR absorption features.

Figure 1 shows the run of carbon-bearing ions for the standard model of IRC + 10216; also shown are the abundances X_3 and X_4 of neutral hydrocarbon molecules with odd and even numbers of carbon atoms ≥ 3 or ≥ 4, respectively. The results are qualitatively similar to Fig. 5 of GLO, and the general conclusions made in GLO about the formation of complex molecules by ion-molecule reactions remain unchanged. Relative to GLO, the main changes (expressed in terms of peak values) are as follows: $x(HCO^+)$ is decreased by about a factor of 3 to $4.5\,10^{-10}$; $x(C_2H_3^+)$ is decreased by a factor of 2 to $1.8\,10^{-10}$, $x(H_2CN^+)$ is increased by more than a factor of 5 to $5\,10^{-9}$, and H_3^+, X_3^+, and X_4^+ are changed by small amounts ($\pm 30\%$). Thus the main change is the large increase in H_2CN^+, which arises from the low temperature enhancement of ionic reactions with HCN. Ions such as $C_2H_3^+$ and HCO^+, whose destruction is strongly influenced by reactions with HCN, are correspondingly reduced in abundance.

The spatial distribution of H_2CN^+ is broader than all the other molecular ions. At small distances, $r < 10^{16}$ cm, it is produced by the cosmic ray ions and at intermediate distances, $10^{16} < r < 10^{17}$ cm, by hydrocarbon ions, particularly $C_2H_2^+$; it is destroyed by dissociative recombination. The large abundance of H_2CN^+ does not imply that it will replace HCO^+ as a potential observational signature for the ionization of C-rich CSEs. The best calculation of the dipole moment of H_2CN^+ is $0.29\,D$ (Botschwina 1986), so that the brightness temperature of the $J = 1 - 0$ transition at 74 GHz (Bogey et al., 1985) will be much less than 1 mK for IRC + 10216. Similarly, the column density of H_2CN^+ is of order 10^{13} cm^{-2}, and its detection in the IR also seems infeasible. There are two additional implications of the
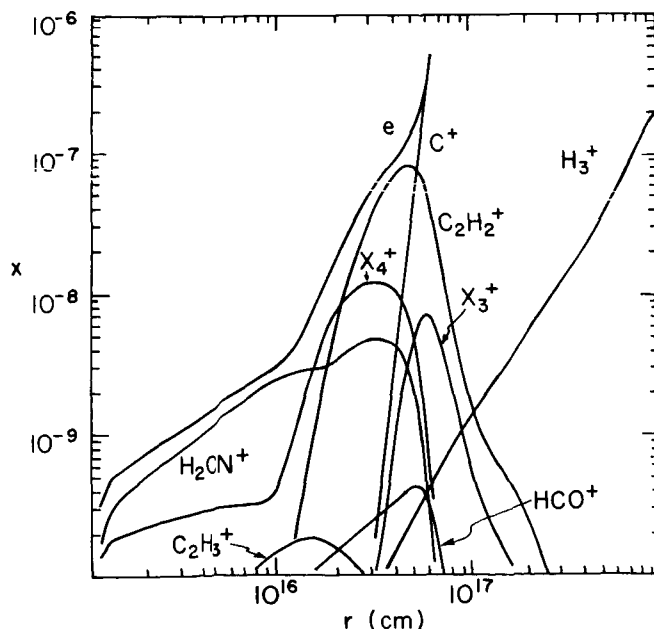

Fig. 1. The spatial distribution of various ions for the standard parameters of Table 1. X_3^+ and X_4^+ represent the total abundance of ions with odd and even numbers of carbon atoms ≥ 3 and ≥ 4, respectively. The abundances refer to the total number of hydrogen nuclei

increased abundance of H_2CN^+, however, which have a bearing on other observable species. The first is an increase in the abundance of HNC implied by Eq. (3), which will be discussed in more detail below. The second is that the production of HC_3N is increased by the low temperature enhancement of reaction No. 10b:

$$C_2H_2^+ + HCN \longrightarrow \begin{cases} H_2CN^+ + C_2H \\ H_2C_3N^+ + H \end{cases}$$
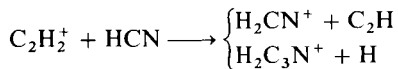
with HC_3N being produced by the dissociative recombination of $H_2C_3N^+$.

In order to test the sensitivity of the results to the kinetic temperature, we have done calculations where the slope and scale of the standard distribution in Table 1 (due to Kwan and Linke 1982) are changed. The main effects come from the temperature dependence of ion-molecule reactions with HCN and of recombination coefficients. The most important observational issue is the peak abundance of HCO^+, which is sensitive to the temperature at the peak. In the standard model, the temperature is 20 K. When it is changed by a factor of two, the peak HCO^+ abundance changes by about 65%, mostly due to the effects of reaction No. 6. If the initial abundance of HCN were reduced (see Sect. 3.3), the change would be smaller. Another ion affected by temperature is $C_2H_3^+$, which is important in the synthesis of C_4H_2 via reaction 11. Again, factor of two changes in temperature lead to abundance changes for $C_2H_3^+$ and for X_4^+ (mainly $C_4H_3^+$) before its peak that are somewhat less than two. It may be noted that the temperature measurement of Sahai and Wannier (1985) for the inner dust envelope ($r = 6\,10^{15}$ cm) are almost a factor of two larger than an extrapolation of the model of Kwan and Linke.

One further point about the chemistry associated with HCN is the substantial rate of production of CNC^+ by reaction No. 14 (Daniel et al., 1986). Using the heats of formation given by these authors, we find that this ion cannot be hydrogenated by reactions with the major H-bearing molecules, H_2, C_2H_2, and HCN. It may undergo condensation reactions with acetylene and produce additional amounts of C_3H and HC_3N. If this is the case, its abundance will be rather small because the reaction with C_2H_2 will dominate dissociative recombination at intermediate distances. Production of C_3H and HC_3N by CNC^+ is unlikely to compete with the more direct channels discussed in GLO which are based on the reactions of C^+ and $C_2H_2^+$ with C_2H_2.

The abundance of C_2H_2 is sufficiently high that it partially shields itself from the external UV radiation. Because photodissociation and photoionization of C_2H_2 are basically continuum processes, the theoretical treatment of self-shielding is relatively straightforward, and the method used by Huggins and Glassgold (1982) for H_2O has been adapted to this case. When C_2H_2 self-shielding is included, some quantitative changes occur in closely related species, e.g. the rise at small distances of C_2H, C_2, X_3, $C_2H_2^+$, and X_3^+ are shifted to slightly larger distances. The abundance of HCO^+ is unaffected. The only species whose peak abundance is changed is $C_2H_3^+$; C_2H_2 self-shielding increases its abundance by about 30%. None of these changes is expected to have any significant observational consequences.

We have also examined the effect of changing the cosmic ray ionization rate ζ. In the standard parameter set of GLO, $\zeta = 5\,10^{-18}$ s^{-1}, consistent with the high energy cosmic ray flux observed in the solar system and with molecular abundances in dense clouds. On the basis of a recent re-analysis of several well

studied diffuse clouds, van Dishoeck and Black (1986) have suggested using a much larger rate, $7\,10^{-17}$ s^{-1}. We have done a calculation for a C-rich CSE in which the only change in the standard model was to increase ζ by a factor of 10 to $5\,10^{-17}$ s^{-1}. Substantial changes in the abundances of cosmic ray generated molecular ions are obtained. For an ion that contributes negligibly to the total ionization, such as H_3^+, HCO^+, or $C_2H_3^+$, the abundance increases linearly with ζ. Because H_2CN^+ is the dominant ion for $r < 10^{16}$ cm, its abundance increases only as $\zeta^{0.5}$ in this region. The production rate of HNC is proportional to $x_e x(H_2CN^+)$ and its abundance scales as ζ at small distances and as $\zeta^{0.5}$ near its peak. The observational implications of a cosmic ray ionization rate larger than "standard" for HCO^+ and HNC will be explored further in the following sections.

3.2. The abundance of HCO^+

Our new results for the spatial distribution of HCO^+ in C-rich CSEs are given in Fig. 2. The solid curves correspond to Fig. 4 of GLO; the three values for the mass loss rate define a realistic range for IRC + 10216, which remains the best studied C-rich CSE. The abundances have been adjusted for the two non-standard cases of $\dot M = 10^{-5}$ and 10^{-4} $M_\odot$ yr^{-1} so that the total loss rates of the progenitor molecules CO, C_2H_2, and HCN are the same as for the standard case, $\dot M = 4\,10^{-5}$ $M_\odot$ yr^{-1}. (Thus the initial abundances have been increased relative to Table 1 by a factor of 4 for $\dot M = 10^{-5}$ $M_\odot$ yr^{-1} and decreased by 2.5 for $\dot M = 10^{-4}$ $M_\odot$ yr^{-1}.) The peak value and the size of the HCO^+ distribution both increase with mass loss rate, but less rapidly than linearly. The calculated antenna temperatures (main beam brightness temperature of a perfect telescope with a gaussian beam)
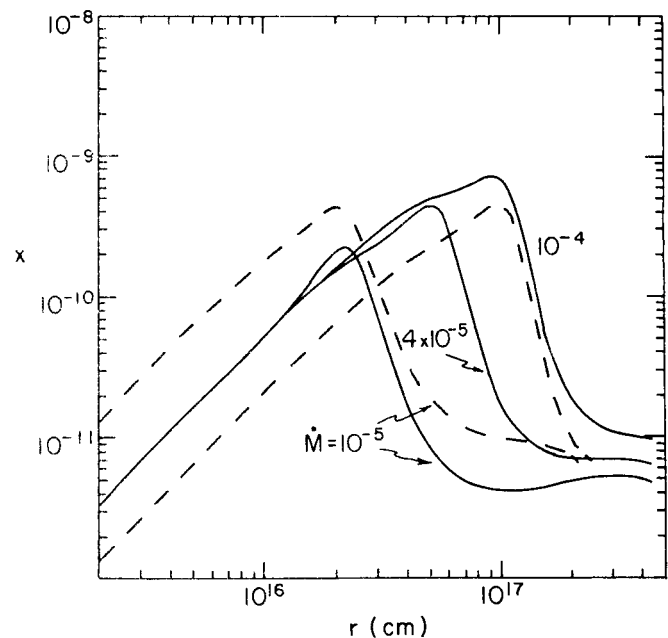

Fig. 2. The spatial distribution of HCO^+ for three values of the mass loss rate. The middle solid curve is the standard model (see Table 1). The other solid curves are for smaller and larger mass loss rates, with the abundances at the base of the envelope scaled as $\dot M^{-1}$. The dashed curves are for the same mass loss rates but with the same abundances as in the standard model

Table 3. Main beam brightness temperatures for the $J = 1 - 0$ line of HCO$^+$ (89 GHz)

Model		T_A(mk) Telescope		
$\dot{M}(M_\odot \, \text{yr}^{-1})$	Abundances[a]	20-m	30-m	45-m
10^{-5}	Scaled	1.6	3.4	6.6
$4 \, 10^{-5}$	Scaled[b]	13	24	38
10^{-4}	Scaled	50	81	114
10^{-5}	Fixed	2.9	6	12
10^{-4}	Fixed	17	28	41

[a] Abundances: scaled means that $\dot{M}$ times the initial abundances of CO, C_2H_2, and HCN are fixed; fixed means the same abundances as in Table 1.

[b] The standard model

for on-source measurements of the $J = 1 - 0$ line of HCO$^+$ near 89.2 GHz are given in Table 3 for three large mm telescopes. The antenna temperature increases with $\dot{M}$ more rapidly than linearly. The dashed curves in Fig. 2 give the spatial distribution of HCO$^+$ for two additional values of the mass loss rate but with abundances fixed at the standard values in Table 1; the corresponding antenna temperatures are given in Table 3. These might be applicable to other C-rich CSEs besides IRC + 10216. When the abundances are kept constant, the HCO$^+$ antenna temperature becomes an even steeper function of mass loss rate.

The HCO$^+$ antenna temperature calculated with the standard model is 24 mK, consistent with the upper limit of 20 mK obtained for IRC + 10216 by Lucas et al. (1986) with the IRAM 30-m telescope. Of course the actual antenna temperature may well be less than this, but another search with the 30-m telescope would require sensitivities at the mK level. The 45-m Nobeyama telescope would be of some help because its larger dish gives a proportional increase in sensitivity in this case, all other things being equal. It would also be of interest to search for HCO$^+$ in other C-rich CSEs with mass loss rates comparable to or larger than that for IRC + 10216 using high sensitivity systems.

We have also considered the effects of varying some of the assumptions in the model in the context of the abundance of HCO$^+$. For example, increasing the cosmic ray ionization rate by 10 (to $5 \, 10^{-17} \, \text{s}^{-1}$), suggested by the analysis of diffuse interstellar clouds by van Dishoeck and Black (1986), increases both the abundance and the antenna temperature by the same factor of 10. Without further adjustments, the model would then be in strong conflict with the IRAM upper limit for HCO$^+$. The consistency between the model and the observations could be restored by reducing the mass loss rate by a factor of 5. However, a mass loss rate for IRC + 10216 smaller than $10^{-5} \, M_\odot \, \text{yr}^{-1}$ would be difficult to reconcile with other molecular measurements, including CO. Another possibility is that the cosmic ray ionization rate varies significantly with position in the Galaxy.

It was emphasized in GLO that the abundance of HCO$^+$ is strongly affected by the ionization of the CSE. In the standard model, the main source of electrons is photoionization of C produced in the C_2H_2 photochain. Increasing the initial abundance of C_2H_2 leads to a reduction in the HCO$^+$ abundance,

but it also increases C_2H, which is already too abundant in the model. Conversely, trying to solve the C_2H problem for IRC + 10216 by reducing the initial C_2H_2 abundance leads to HCO$^+$ abundances in conflict with the IRAM upper limit and possibly with IR absorption measurements.

If there were another source of electrons, independent of the C_2H_2 photochain, then HCO$^+$ could be reduced further without aggravating the C_2H_2/C_2H situation (unless the new species destroys C_2H_2 and C_2H). The CO photochain deserves consideration, but strong self-shielding limits the production of C$^+$ to beyond the region of large HCO$^+$ abundance. Yet another possibility is that there is another neutral species entering the outer envelope that is photoionized. To be effective, the abundance of this species must be $> 10^{-5}$ in the standard model and its photoionization rate $> 10^{-10} \, \text{s}^{-1}$. Heavy elements like S, Si, Fe, and Mg are candidates, but they are likely to be depleted onto dust grains. An interesting possibility is free, atomic carbon that might be left as a residue from the process of dust formation in the inner envelope. Our calculations suggest that an initial C abundance of 10^{-5} could reduce the peak HCO$^+$ abundance by a factor of 2, assuming that C does not react with C_2H_2 and C_2H in the inner CSE. The present upper limit to the abundance of C in IRC + 10216, obtained from attempts to detect the 605 micron line with the NASA 3-m IRTF (Beichman et al., 1983), is an order of magnitude larger. Beichman et al. have reported a detection of this line in another C-rich CSE, CRL 2688 (the Egg Nebula) with the NASA 0.94-m KAO at a level that suggests C/CO > 4 in this object. The relation between abundances in CRL 2688 and IRC + 10216 is unclear at present because these two objects are so different in structure and dynamics. For example, CRL 2688 is a bipolar nebula with an embedded star of spectral type F5 Ia (Cohen and Kuhi 1977). The emission at 2.12 microns of the $v = 1 - 0$ S(1) line of H_2 in CR 2688 has been interpreted in terms of shocks produced by a stellar wind (Beckwith et al., 1984). Perhaps a large C/CO ratio is also produced by these shocks. It is noteworthy that the optical spectrum (Cohen and Kuhi 1977), is characterized by emission of the C_2 molecule.

3.3. The abundance of HNC

The observed values of the ratio HCN/HNC in C-rich CSEs have been interpreted in terms of a freeze-out model (e.g. McCabe et al., 1979), where $x(HCN)/x(HNC) = \exp(\Delta E/kT)$ and $\Delta E = 0.67 \, \text{eV}$ ($\sim 7800 \, \text{K}$) is the energy difference between the ground states of HNC and HCN. Typical values for this ratio are $6 \, 10^6$, 2500, and 200 for values of the freeze out temperature $T = 500$, 1000, and 1500 K, respectively. If the relatively large HCN/HNC ratio observed for IRC + 10216 is interpreted in this way, the freeze out must occur at a fairly high temperature, $T \sim 1400 \, \text{K}$. However, it is unlikely that freeze out actually occurs at such a high temperature because the reactions.

$$HCN + H \underset{b}{\overset{a}{\rightleftharpoons}} CN + H_2 \underset{d}{\overset{c}{\rightleftharpoons}} HCN + H \quad (3)$$
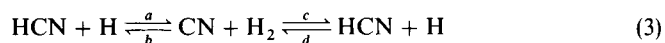
are expected to be operative throughout a good part of the outer CSE. Reaction c is known to have a moderate activation energy, $k_c = (1.0 \pm 0.3) 10^{-11} \exp(-2670/T) \, \text{cm}^3 \, \text{s}^{-1}$ (Albers et al., 1974), but the activation energy of reaction b is unknown. If it is the same as that for reaction c, then the conversion of HNC to HCN through the reactions in Eq. (3) would not freeze out
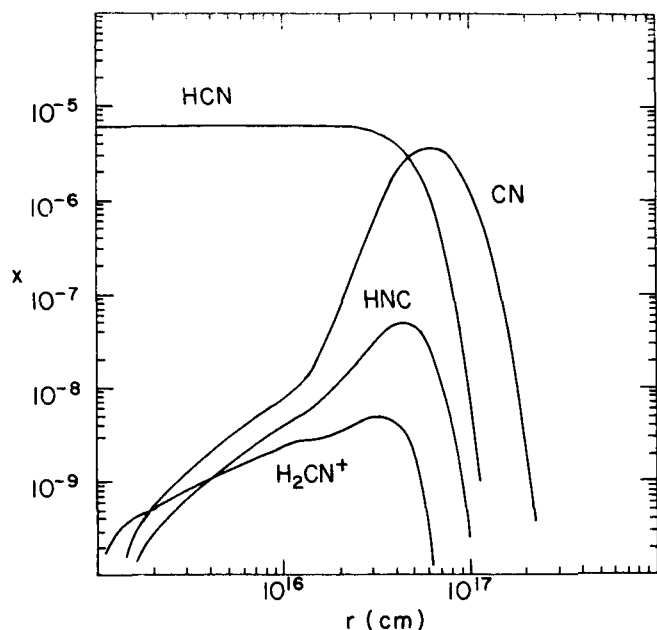
Fig. 3. The spatial distribution of the HCN photochain for the standard parameters of Table 1

until T had decreased to about 500 K, assuming that the ratio of atomic to molecular hydrogen is $\gtrsim 10^{-3}$ (Glassgold and Huggins 1983), which implies a much larger HCN/HNC ratio than is observed for IRC + 10216. Even if the activation energy of reaction a were twice that of reaction c, the freeze-out would not occur until T had decreased to ~ 900 K, which would yield HCN/HNC ~ 6000 if H/H$_2 \gtrsim 10^{-3}$.

The large value of HNC/HCN in IRC + 10216 has a natural interpretation in the photochemical model. As described in Sect. 2, H$_2$CN$^+$ is formed by proton transfer from other molecular ions to HCN, and HNC is then produced by dissociative recombination according to Eq. (2). The results of our model calculations are shown in Fig. 3 for the standard parameters and a branching ratio, $b_2 = 0.25$. The abundance ratio varies with distance from the star because HCN and HNC vary in different ways. Thus going across the peak of HNC in Fig. 3, HCN/HNC varies from 200 to 40. It is noteworthy that the spatial distribution of HNC is smaller than that of CN, e.g. the peaks of

HNC and CN in Fig. 3 occur at 4 and 6 10^{-16} cm, respectively. There is some observational indication of this effect (Olofsson et al., 1982, Truong-Bach et al., 1986). It would be interesting to test this prediction of the photochemical model by making maps of both HNC and CN with a large telescope or interferometer. The mean abundance ratio is not very sensitive to mass loss rate; it does decrease slowly with $\dot{M}$. More important, the size of the HNC distribution increases with increasing $\dot{M}$.

Table 4 gives the predicted antenna temperatures for H^{13}CN and HNC for the models discussed for HCO$^+$ in connection with Table 3; HCN is not given because the large optical depths for the relevant mm transitions make it much less useful than its isotopic forms. The calculations are based on the value of 40 given by Wannier (1985) for the ^{12}CO/^{13}CO isotope ratio, which is in substantial agreement with more recent measurements by Kahane et al. (1987). The IR lines of H^{13}CN and HNC have also been assumed to be optically thin. It is important to stress that the IR line strengths of HNC are somewhat uncertain and have been represented by a single line with IR dipole moment = 0.16 D. It should also be noted that the 1 $-$ 0 population of H^{13}CN appears to be inverted in the inner part of the CSE, which makes the calculated T$_A$ sensitive to the model parameters. We first consider the ratio of H^{13}CN to HNC antenna temperatures, in order to reduce the sensitivity of the conclusions to various uncertainties in the analysis. For a 30-m telescope, this ratio is 6.2 for the standard case; it increases with $\dot{M}$, but less rapidly than linearly. This result is in good agreement with the ratio of 7.0 recently determined for IRC + 10216 with the IRAM telescope (Kahane et al., 1987). The standard model also agrees with the Onsala ratio of ~ 4 (Olofsson et al., 1982). If we consider the absolute antenna temperatures, the model predicts values which are too large by a factor of two for both HNC and H^{13}CN. Close agreement with both values could be achieved by reducing the initial abundance of HCN or both b_1 and b_2 by a factor of two, all of which are permitted by the uncertainties in these quantities. Changing the mass loss rate is not called for, because it affects H^{13}CN and HNC differently.

Bieging et al. (1984) have derived a smaller abundance for HCN in IRC + 10216 than our standard model from mm interferometric measurements with a 9″ synthesized beam. They also find a smaller abundance in the interior of the envelope (inside 9″) relative to the outside. Such a decrease in abundance at small distances would have a small effect on the predictions of the photochemical model for the spatial distribution of HNC and

Table 4. Main beam brightness temperatures for the $J = 1 - 0$ lines of H^{13}CN and HNC

Model		T_A(K)			
$\dot{M}(M_\odot \, \mathrm{yr}^{-1})$	Abundances[a]	20-m telescope		30-m telescope	
		H^{13}CN	HNC	H^{13}CN	HNC
10^{-5}	Scaled	1.8	0.8	3.9	1.7
$4 \, 10^{-5}$	Scaled[b]	6.8	1.4	13.6	2.2
10^{-4}	Scaled	4.1	2.1	10.4	3.2
10^{-5}	Fixed	0.56	0.13	1.2	0.28

[a] See the explanation in Table 3.
[b] The standard model

CN, because these distributions peak at larger distances. When the exterior abundance of Bieging et al. is scaled to our adopted distance of 200 pc, the result is 1/3 of the abundance of the standard model. Taking into account that $\sim 1/2$ of the emission is resolved out in the interferometric measurement, we suggest that the exterior HCN abundance, before it is reduced by photo-destruction, is $\sim 3\,10^{-6}$ on the basis of the work of Bieging et al. (1984). As we discussed above, this abundance produces good agreement between the photochemical model and the single dish measurements of $H^{13}CN$ and HNC. Thus our best estimate of the abundance of HCN for the IRC + 10216 CSE is $3\,10^{-6}$, down by a factor of two compared with the standard model. The column density into 10^{15} cm ($1/3''$ at 200 pc), which might be the beginning of the dust shell is $6\,10^{17}$ cm^{-2}, a factor of 2.5 smaller than the fairly uncertain value obtained by Hall and Ridgway (1978) on the basis of IR absorption measurements.

We conclude this discussion of HNC in C-rich CSEs with a brief comment about the role of the cosmic ray ionization rate. As remarked earlier, the abundance increases as ζ in the interior of the envelope and as $\zeta^{0.5}$ near the peak. We have calculated the change in the HNC antenna temperature when the standard cosmic ray ionization rate is increased by 10, and find that it increases by about a factor of 4. Thus increasing ζ produces a smaller $H^{13}CN/HNC$ ratio, and tends to destroy the reasonable agreement of the standard model with the observations of IRC + 10216.

4. Conclusion

In this paper we have given an improved version of the photo-chemical model for C-rich CSEs. Although strongly founded on our previous work (GLO), our goal here has been to develop a more quantitative model suitable for analyzing data relevant to molecular ions, using IRC + 10216 as a test case. The model has been improved by incorporating new understanding of several basic physical processes, in particular the temperature dependence of ion-molecule reaction rates and the self-shielding of CO. The observational data of interest include the new upper limit to the antenna temperature of the $J = 1 - 0$ line of HCO$^+$ in IRC + 10216 (Lucas et al., 1986) and the large HCN/HNC ratio observed in C-rich CSEs, particularly the accurate values for IRC + 10216 (Olofsson et al., 1982, Kahane et al., 1987).

The new calculations show quantitative but not qualitative differences with GLO. The largest changes arise from the temperature dependence of ion-molecule reactions with HCN. The final result of the analysis is that both the upper limit for HCO$^+$ and the HNC/HCN ratio in IRC + 10216 can be accounted for in our standard model for this object, using the same parameters as GLO. This parameter set is based on the analysis of CO observations by Kwan and Linke (1982) and infrared absorption measurements of C_2H_2 and HCN. The general conclusion of GLO, that the chemical activity of the intermediate regions of C-rich CSEs is basically ion-molecule in character, is strengthened by the increased role of HCN, which leads to larger abundances for complex, N-bearing molecules.

The abundance of HCO$^+$ in IRC + 10216 (peak abundance $4.6\,10^{-10}$ in the standard case) may be still too large. Several possibilities for reducing it have been discussed in this paper and in GLO. The first is decreasing the mass loss rate $\dot{M}$. The HCO$^+$ antenna temperature is fairly sensitive to $\dot{M}$ (varying as $\dot{M}^{4/3}$)

and, reducing $\dot{M}$ by 2 for example, reduces $T_A(HCO^+)$ by a factor of 2.5 to 10 mK. One motivation for considering smaller values for $\dot{M}$ is that IRC + 10216 may be closer than we have assumed (200 pc), e.g. Zuckerman et al. (1986) have recently suggested that the distance might be 100–150 pc. For this distance, $\dot{M}$ would have to be reduced by a factor of a few in order to maintain the HCO$^+$ brightness temperature at the same value as the standard model. Yet another way of reducing the abundance of HCO$^+$ is to increase the ionization in the neighborhood of its peak abundance. We suggested one such scenario where a relatively small amount of free atomic carbon (of order 10^{-5}) is left over from the process of dust formation and then photoionized by interstellar radiation. Another possibility is that the cosmic ray flux into the CSE is reduced by the action of strong magnetic fields. Evidence for significant magnetic fields in O-rich CSEs now exists from measurements of the Zeeman effect in OH masers (Cohen 1987). We have also pointed out that increasing the cosmic ray ionization rate to the level used in the recent analysis of diffuse interstellar clouds (van Dishoeck and Black 1986), would lead to serious disagreement between the model and the limits on HCO$^+$ set by observations with the IRAM 30-m telescope (Lucas et al., 1986).

At the present time, the photochemical model provides the most convincing description of the chemistry of C-rich CSEs. It embodies the well founded ideas of thermal equilibrium for saturated molecules, but includes the inevitable destruction of circumstellar molecules by interstellar UV radiation. The model allows for the fact that radicals do not necessarily freeze out far out in the CSE, and its basic photochemical nature leads to a strong ion-molecule chemistry at intermediate distances, consistent with the low temperatures of these envelopes. One serious problem of the photochemical model is that it predicts about one order of magnitude too much C_2H in IRC + 10216, if IR absorption measurements are used to determine the initial abundance of C_2H_2. It would be of great interest to determine whether a similar problem occurs for other C-rich envelopes. Although C_2H has been detected in the bipolar nebula CRL 2688 (Huggins et al., 1984; Lucas et al., 1986), its abundance relative to C_2H_2 is unknown for this object. Clearly the model requires further careful testing, and many observational opportunities are now becoming feasible with the increasing availability of systems capable of high sensitivity observations with high spatial resolution.

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